Sorption isotherms of celery leaves (*Apium graveolens* var. *secalinum*)

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Abstract: Sorption isotherms provide important information for the drying process and storage of foodstuffs. The desorption isotherms of celery leaves at three temperatures (25, 40 and 50℃) as well as their adsorption isotherm at 25℃ were experimentally determined by means of the static gravimetric method, using eight saturated salt solutions with relative humidities in the range from 11% to 84%. Six mathematical models (Halsey, Oswin, Henderson, GAB, Peleg and BET) were fitted to the data. The Peleg model resulted in the lowest error in all cases. A modification of the Peleg model was attempted to incorporate the effect of temperature in the desorption process. The fitting was satisfactory, providing a single equation for calculation of the equilibrium conditions within the studied temperature range.

Keywords: sorption, isotherms, celery, model

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1 Introduction

Celery (*Apium graveolens* L.) is a plant species of the family Apiaceae. Leaf celery (*Apium graveolens* L. var. secalinum), also known as cutting celery, is a variety in which the usable parts are the dark-green, glossy leaves on long, thin leaf petioles, presenting a strong celery flavor. They may be eaten fresh or processed, mainly frozen or dried (Rozek, 2007). Although not as well known as celeriac (*Apium graveolens* L. var. *rapaceum*), it is an economically important herb in Germany, with 136 ha of cultivated area in 2003 (Hoppe, 2005).

In general leaves require less time and energy for drying than other parts of plants, which makes celery leaves more suitable for the drying process compared to the stalk or root parts commonly used in the other varieties.

Sorption isotherms define the hygroscopic equilibrium between the relative humidity and moisture content at a given temperature. Thus, they provide important information for the drying process and storage of foods and other products.

2 Materials and methods

2.1 Plant materials

Leaf celery (*Apium graveolens* var. *secalinum*) was sowed in pots in mid March and kept in a greenhouse until late May, when the plants were moved into the research field of the Agricultural Engineering Department of Kassel University in Witzenhausen in the year 2009. Plants were harvested manually and leaves separated immediately before each trial.

2.2 Experimental procedure

Desorption isotherms were determined at 25, 40 and 50℃, whereas adsorption at 25℃ only. In all cases， the static gravimetric method was used to reach the equilibrium moisture content. Eight glass jars were partially filled with saturated salt solutions (Table 1).

The solutions were prepared by dissolving the salts in distilled water at 50℃ until, after thorough mixing, salt cristals remained visible. The sample weight was about 0.5 g fresh product for desorption and 0.25 g for

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adsorption. Before the adsorption process fresh samples were dehydrated in a dessicator over P_2O_5 for 15 days at an ambient temperature (Arabhosseini et al., 2006; Menkov, 2000; Saravacos, Tsiourvas and Tsami, 1986).

Table 1 Relative humidity of saturated salt solutions

Salt	Equilibrium relative humidity		
	25℃	40℃	50℃
LiCl	0.113	0.112	0.111
CH_3COOK	0.225	0.201	0.189
$MgCl_2$	0.328	0.316	0.305
K_2CO_3	0.438	0.432	0.409
$Mg(NO_3)_2$	0.529	0.484	0.460
$NaNO_2$	0.640	0.615	0.598
NaCl	0.753	0.747	0.744
KCl	0.843	0.823	0.812

The samples were introduced in perforated metal recipients, which were placed inside the jars, above the salt solutions. The jars were then hermetically closed and placed inside an oven with forced air circulation where the temperature was kept constant for the duration of the trial. In jars where the relative humidity was over 60%, a test tube with thymol crystals was introduced in order to prevent spoilage (Arabhosseini et al., 2006; Menkov, 2000). The samples were weighed every three days with a Sartorius A200S analytic scale (resolution 0.0001 g) until the difference between consecutive measurements was less than 0.001 g for all jars. To avoid a concentration gradient within the salt solutions, these were stirred at the time of each weighing (Arabhosseini et al., 2006; Kouhila et al., 2000). Equilibrium moisture content was determined using the oven method (105℃ for 24 h). Each treatment was carried out two times and the averages were reported.

2.3 Model fitting

From the many mathematical models found in the literature to describe sorption isotherms, six were selected and fitted to each temperature's results (Table 2). The statistics software SPSS 17 was used to fit the models to the data using the nonlinear regression function. To be sure that the parameters obtained were the optimal, each regression was repeated with different starting parameter values.

Table 2 Sorption isotherm models fitted to the experimental data

Model	Equation	Source
Halsey	$M=\left[\dfrac{-a}{\ln(RH)}\right]^{\frac{1}{b}}$	(Iglesias and Chirife, 1982)
Oswin	$M=a\left(\dfrac{RH}{1-RH}\right)^{b}$	(Iglesias and Chirife, 1982; Park, Vohnikova and Reis Brod, 2002)
Henderson	$M=\left[\dfrac{-\ln(1-RH)}{a}\right]^{\frac{1}{b}}$	(da Silva et al., 2004; Iglesias and Chirife, 1982)
GAB	$M=\dfrac{abcRH}{(1-bRH)(1-bRH+bcRH)}$	(ASABE, 2008)
Peleg	$M=aRH^{c}+bRH^{d}$	(Peleg, 1993)
BET	$M=\dfrac{abRH}{(1-RH)(1+RH(b-1))}$	(Iglesias and Chirife, 1982; Liendo-Cardenas, Zapata-Norena and Brandelli , 2000)

Note: where, M is the equilibrium moisture content d.b.; RH the equilibrium relative humidity; a, b, c, d the models' parameters.

The goodness of fit of the equations was evaluated using the coefficient of determination R^2 together with the mean relative error, MRE, and the standard error of the estimate, SEE (Mehta and Singh, 2006; Soysal and Öztekin, 1999; Sun, 1999):

$$MRE \qquad \frac{1}{n}\sum_{i=1}^{n}\frac{|M-\hat{M}|}{M}$$

$$SEE \qquad \sqrt{\frac{\sum_{i=1}^{n}(M-\hat{M})^2}{n-p}}$$

Where, n is the number of experimental points; p is the number of parameters.

Additionally, residuals were plotted against relative humidity and visually assessed for randomness (Menkov, 2000; Soysal and Öztekin, 1999).

3 Results and discussion

Figure 1 presents the experimental desorption data for celery leaves at the studied temperatures. The data points describe the typical S-shape curves. Also as expected, the equilibrium moisture content decreased with increasing temperature, although at high relative humidities these differences seemed to disappear. Figure 2 shows the desorption and adsorption results at 25℃. A hysteresis effect was noticeable, particularly at relative humidities above 0.5. Similar trends have also been found for tarragon and citrus leaves (Arabhosseini et al., 2006; Jamali et al., 2006).

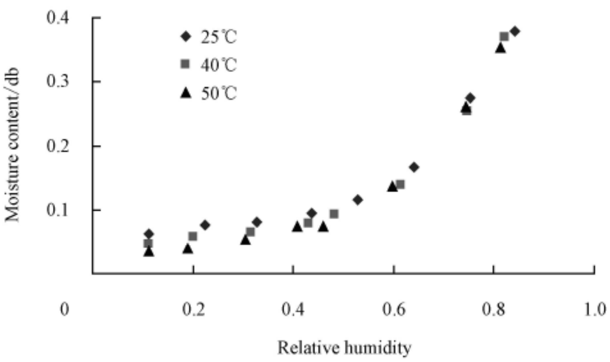

Figure 1 Experimental desorption data for celery leaves at 25, 40 and 50℃

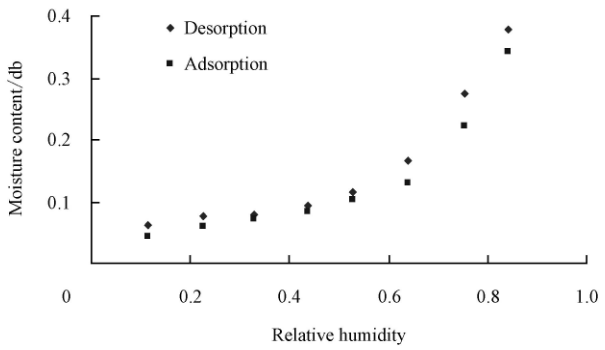

Figure 2 Experimental adsorption and desorption data for celery leaves at 25℃

The results of the fitting of the isotherm models appear in Table 3. As can be seen, the Halsey, the GAB and the Peleg models were the ones that best described the experimental results, as measured by the coefficient of determination and both the MRE and SEE. However, the Peleg model was consistently the best in all cases. Other studies have also found this model to be the most accurate (Bahloul, Boudhrioua and Kechaou, 2008; da Silva et al., 2004; Park, Vohnikova and Reis Brod, 2002). Figure 3 shows the experimental desorption data at 40℃ together with the predicted curves using the three best fitting models, namely the Halsey, GAB and Peleg. Figure 4 presents the residual plots for the Halsey, GAB, Peleg and BET models. Only the Peleg model showed randomly distributed residuals with no clear pattern. Although this model is semi-empirical and has the most parameters, its equation is fairly simple and lends itself well to the most practical food applications of sorption isotherms (Peleg, 1993).

Assuming a storage temperature of 25℃ and a safe water activity of 0.6, and using the Peleg equation and its corresponding coefficients for adsorption, celery leaves should be dried to a moisture content of 12% db to ensure its microbiological stability over long periods of time.

Table 3 Regression coefficients and goodness of fit for the applied models

	Model	Models' coefficients				R^2	*SEE*	*MRE*
		a	*b*	*c*	*d*			
25℃ Desorption	Halsey	0.0532	1.2198			0.986	0.0145	0.1010
	Oswin	0.1250	0.6571			0.974	0.0199	0.1554
	Henderson	4.6637	0.9203			0.948	0.0279	0.2232
	GAB	0.0628	0.9949	31.6816		0.987	0.0156	0.0774
	Peleg	0.6265	0.0854	4.3336	0.1226	0.998	0.0063	0.0286
	BET	0.0613	41.6313			0.986	0.0143	0.0704
40℃ Desorption	Halsey	0.0720	1.0005			0.993	0.0101	0.1050
	Oswin	0.1065	0.7997			0.982	0.0166	0.1765
	Henderson	3.8022	0.7600			0.962	0.0244	0.2499
	GAB	0.0526	1.0461	15.3832		0.993	0.0112	0.0757
	Peleg	0.7897	0.0892	5.2268	0.2925	1.000	0.0016	0.0119
	BET	0.0676	4.2605			0.987	0.0141	0.1405
50℃ Desorption	Halsey	0.0805	0.9284			0.995	0.0089	0.0669
	Oswin	0.1015	0.8544			0.992	0.0113	0.1409
	Henderson	3.5940	0.7227			0.983	0.0165	0.2273
	GAB	0.0673	1.0163	2.7691		0.992	0.0122	0.1196
	Peleg	0.7125	0.0748	4.4236	0.3562	0.999	0.0042	0.0230
	BET	0.0739	2.2154			0.992	0.0113	0.1319
25℃ Adsorption	Halsey	0.0497	1.1406			0.994	0.0107	0.0716
	Oswin	0.1017	0.7049			0.981	0.0153	0.1445
	Henderson	4.8718	0.8549			0.951	0.0242	0.2350
	GAB	0.0506	1.0127	23.4250		0.996	0.0073	0.0322
	Peleg	0.6943	0.1192	6.4111	0.4668	0.999	0.0044	0.0180
	BET	0.0539	14.9156			0.995	0.0074	0.0467

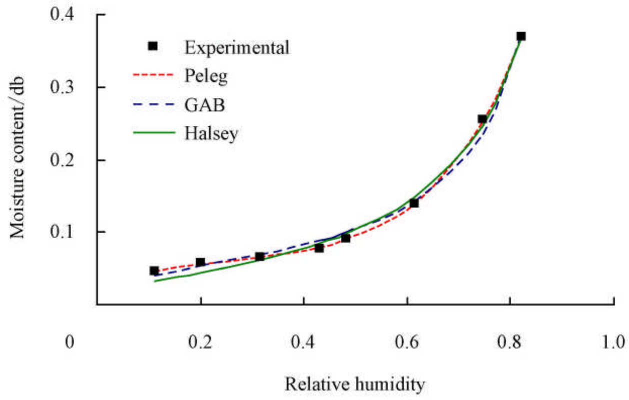

Figure 3 Desorption isotherms of celery leaves at 40℃ as predicted by the Peleg, GAB and Halsey models

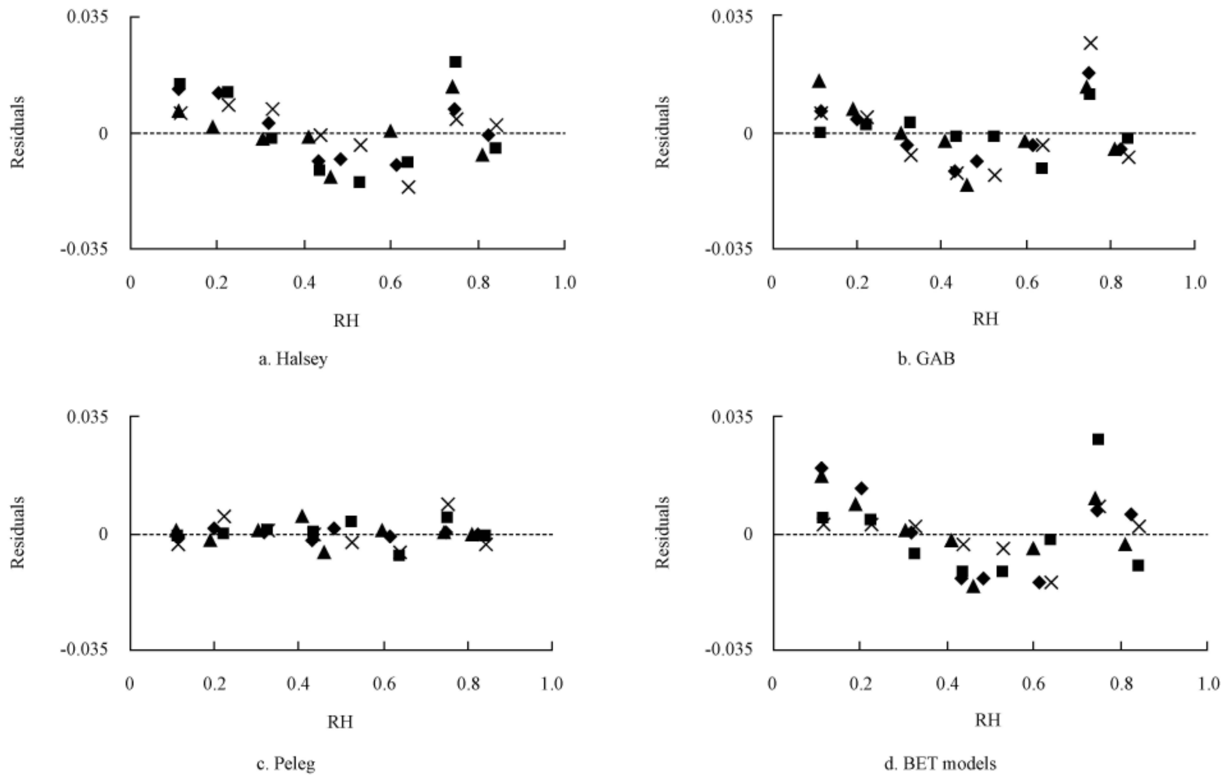

Figure 4 Residual plots for Halsey, GAB, Peleg and BET models

In order to incorporate the effect of temperature in the isotherm equation, a modification of the Peleg model was attempted as follows:

Modified Peleg $M=(a+bT)RH^c+(d+eT)RH^f$

Where, T is the temperature in ℃. The calculated regression parameters were in this case 0.5006, 0.0052, 4.5595, 0.1299, -0.0013 and 0.2102, respectively. The coefficient of determination R^2, the *MRE* and the *SEE* were 0.998, 0.0390 and 0.0052, respectively, resulting in a very good fit, whose predicted curves at the studied temperatures resemble closely those predicted individually by the original model. Thus, this modified model can be used as a single equation to estimate the equilibium conditions of celery leaves in the studied temperature range.

4 Conclusions

The sorption isotherms of celery leaves followed the usual trends of shape and temperature dependance. For their storage at 25℃ or less, a maximum moisture content of 12% db must be reached. From the six models tested, the Peleg model with four parameters offered the smallest error in all cases. A modified version of this model to include the effect of temperature fitted well to all the desorption data, resulting in an equation with six parameters, from which the equilibrium conditions at any temperature from 25℃ to 50℃ can be estimated. These results will serve to model the thin-layer drying behavior of celery leaves at various air temperatures and relative humidities.

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